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(54) Title: DOPO-DERIVED FLAME RETARDANT AND SYNTHETIC HYDROGARNETS FOR EPOXY RESIN COMPOSITIONS

(57) Abstract: This invention relates to synthetic hydrogarnets and 9,10-Dihydro-9-Oxa-10- Phosphaphenantrene-10-oxide derived additive flame-retardants, which are useful in epoxy resin compositions. The epoxy resin compositions may be used in making prepregs or laminates for printed wiring boards and composite materials.

**DOPO-DERIVED FLAME RETARDANT AND SYNTHETIC HYDROGARNETS
FOR EPOXY RESIN COMPOSITIONS**

TECHNICAL FIELD

5 This invention relates to synthetic hydrogarnets and 9,10-Dihydro-9-Oxa-10-Phosphaphenantrene-10-oxide derived additive flame-retardants, which are useful in epoxy resin compositions. The epoxy resin compositions may be used in making prepregs or laminates for printed wiring boards and composite materials.

BACKGROUND

10 Epoxy resins are employed for a wide range of applications such as electronic components, electrical equipment, automotive parts and sporting equipment since the epoxy resins have desirable properties such as adhesiveness, heat resistance and moldability. Flame-retardant agents, in particular brominated epoxy resins compounds are employed for copper-clad laminates and sealants that are used in electronic components and electrical equipment. However, halogen-containing compounds cause concerns about environment and human safety, and therefore flame-retardant agents that are more environmentally friendly are
20 desirable.

Types of flame retardants that are perceived to be more environmentally friendly include organo-phosphorous flame retardants. In the field of epoxy resins and laminates, organo-phosphorous flame retardants with reactive groups, such as those derived from 9,10-Dihydro-9-Oxa-10-Phosphaphenantrene-10-oxide (DOPO), are typically used in epoxy resin
25 formulations because they react with the epoxy to form a phosphorus-modified epoxy resin. The technology for producing phosphorus-modified epoxy resins and their uses, including their use in forming prepregs, laminates and copper-clad laminates is well known in the art. See for example U.S. Pat. Nos. 5,036,135; 5,364,893; 5,376,453; 5,587,243; 5,759,690; 5,817,736, 6,291,626 B1; 6,291,627 B1; 6,296,940 B1; 6,353,080 B1; 6,403,220 B1;
30 6,403,690 B1; 6,486,242 B1; and WO 01/42359 A1 as published in English on June 14, 2001.

However, "additive" organophosphorus flame retardants, which do not have reactive groups, are typically not used in epoxy formulations, since it is believed that covalent bonding between the epoxy resin and a reactive organophosphorus flame retardant are needed
35 to provide high glass transition temperatures and dimensional stability.

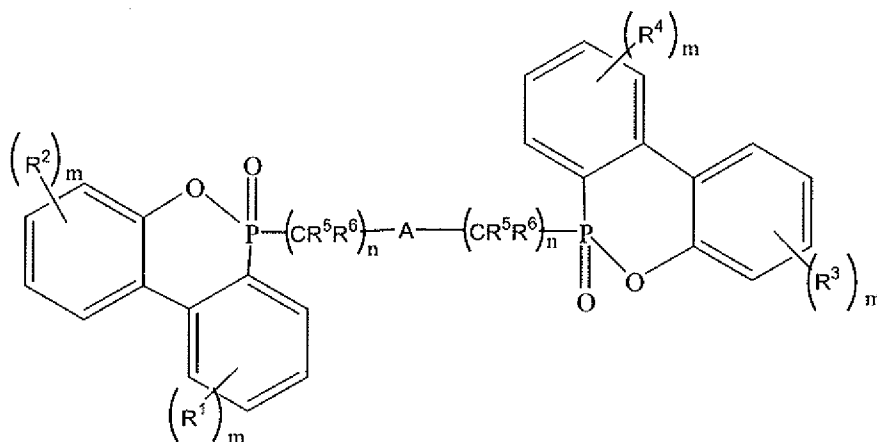
Commonly used mineral flame retardants for polymers such as aluminum trihydroxide (ATH), magnesium hydroxide (MDH) and silica have limited efficiency and use in epoxies. Some mineral flame retardants require high loadings to pass relevant flame tests. In some cases, even when used at highest loadings, certain flame tests are too demanding for the mechanical, thermal, rheological or electrical properties of the final product. For example ATH starts to decompose at about 200°C, which limits the application to epoxies that are processed at low temperatures. Likewise, silica is a very abrasive material, and quickly dulls the drilling bits that are required to drill holes in the printed wiring boards.

It would be of considerable advantage to the art if a way could be found of providing a new combination of flame retardants having high flame retardant efficiency that would also meet the demanding mechanical, thermal, rheological or electrical properties needed for epoxy applications.

SUMMARY OF THE INVENTION

The present invention relates to a flame retardant epoxy composition comprising:

- (i) an epoxy compound;
- (ii) a di-dopo compound having the following structure:



Formula I

wherein A is a direct bond, C₆-C₁₂ aryl, C₃-C₁₂ cycloalkyl, or a C₃-C₁₂ cycloalkenyl, wherein said cycloalkyl or cycloalkenyl may be optionally substituted by a C₁-C₆ alkyl; each R¹, R², R³ and R⁴ are independently hydrogen, C₁-C₁₅ alkyl, C₆-C₁₂ aryl, C₇-C₁₅ aralkyl or C₇-C₁₅ alkaryl; or R¹ and R² or R³ and R⁴ taken together can form a saturated or unsaturated cyclic ring, wherein said saturated or unsaturated cyclic ring may be optional substituted by a C₁-C₆ alkyl;

each m is independently 1, 2, 3 or 4

each R⁵ and R⁶ are independently hydrogen or a C₁-C₆ alkyl;

each n is independently 0, 1, 2, 3, 4 or 5;

with the proviso that when A is aryl or a direct bond, n can not be 0; and

5 (iii) a synthetic hydrogarnet having the empirical formula:

(A) $M^{II}_3M^{III}_2(OH)_{12-4x}(SiO_4)_x$ wherein M^{II} is a Group IIA metal atom, M^{III} is a Group IIIA metal atom, and x is a number in the range of about 0.05 to about 1.5; or

(B) $M^{II}_3M^{III}_2O_y(OH)_{12-5y}(PO_4)_y$ wherein M^{II} and M^{III} are as defined in (A), and y is a number in the range of about 0.05 to about 1.5; or

(C) $M^{II}_3M^{III}_2O_y(OH)_{12-5y-4x}(PO_4)_y(SiO_4)_x$ wherein M^{II} and M^{III} are as defined in (A), wherein x is as defined in (A), and wherein y is as defined in (B), with the proviso that the sum x + y is in the range of about 0.05 to about 1.5; or

(D) $M^{II}_3M^{III}_2(OH)_{12}$ wherein M^{II} and M^{III} are as defined in (A).

15

DETAILED DESCRIPTION OF THE INVENTION

Synthetic hydrogarnet

20 This application provides, among other things, a synthetic hydrogarnet flame retardant comprised of synthetic hydrogarnet optionally modified by inclusion of silicate and/or phosphate ions in its crystal structure.

One embodiment of this invention is a synthetic hydrogarnet having the following formula: $M^{II}_3M^{III}_2(OH)_{12}$.

25 Another embodiment of this invention is a synthetic hydrogarnet characterized by (i) having the empirical formula $M^{II}_3M^{III}_2O_y(OH)_{12-5y-4x}(PO_4)_y(SiO_4)_x$ wherein M^{II} is one or a mixture of more than one alkaline earth metal, preferably Ca; and x and y are numbers in the range of 0 to about 1.5, with x + y in the range of 0 to about 1.5, preferably in the range of about 0.05 to about 1.5; a more preferred range is about 0.1 to about 1.5; even more preferred is about 0.05 to about 1.2.

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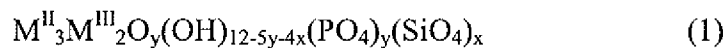
The synthetic hydrogarnet may also have the following properties:

a) a median particle size, d₅₀, in the range of about 0.1 to about 10 μm, or 0.25 to about 5 μm, or 0.25 to about 2.0 μm, or 0.25 to about 1.5 μm as determined by laser diffraction;

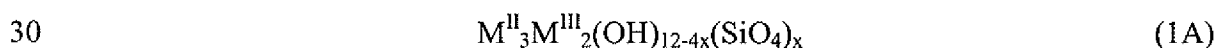
- b) a surface area in the range of about 0.5 to about 30 m²/g as determined by BET, preferably between about 1 to about 30 m²/g, preferably between about 0.5 to about 15 and between about 1 to about 15 m²/g, even more preferably between about 1 to about 10 or between about 2 and about 10 m²/g; or
- 5 c) a TGA temperature for a 2% water loss of >230°C, preferably >240°C, more preferably >250°C at a heating rate of 1°C per minute and after predrying at 105°C during a period of 4 hours.

The synthetic hydrogarnets may be further characterized by having a surface moisture content of <0.7 wt%, preferably <0.5 wt%, as determined by infrared moisture balance at 10 105°C, and a sodium oxide content of <0.5 wt% as determined by flame photometry.

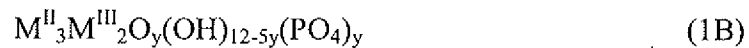
As noted above, the synthetic hydrogarnets can be represented by the following general formula (1):



15 where M^{II} is a Group IIA metal atom, typically Ca, Sr, or Ba, or a mixture of at least two of these, or a mixture of any one or more of these with a minor proportion (*i.e.*, less than about 50% by weight) of Mg; M^{III} is a Group IIIA metal atom, especially aluminum, but which may be in admixture with small amounts (*e.g.*, less than about 20 % by weight) of B, Ga, In, or Tl, or a mixture of any two or more of these; and where x and y are numbers in the range of 0 to 20 about 1.5, with x + y in the range of 0 to about 1.5, preferably in the range of about 0.05 to about 1.5, more preferably in the range of about 0.1 to about 1.5, even more preferred is about 0.05 to about 1.2. The presence of trace amounts of other metal atoms that do not adversely affect the flame retardant and thermal stability properties of the flame retardant can 25 be present. When no silicon or phosphorus source is used in synthesizing the product, the product can be represented by the formula M^{II}₃M^{III}₂(OH)₁₂, where M^{II} and M^{III} are as in formula (1) above. When no phosphorus source is used in synthesizing the product, the synthetic hydrogarnet can be represented by the following general empirical formula:

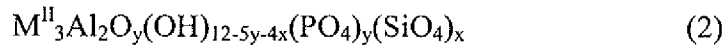


wherein M^{II} and M^{III} are as in formula (1) above, and x is in the range of about 0.05 to about 1.5, preferably in the range of about 0.1 to about 1.5, more preferably in the range of about 0.05 to about 1.2. When no silicon source is used in synthesizing the product, the synthetic 35 hydrogarnet can be represented by the following general empirical formula:

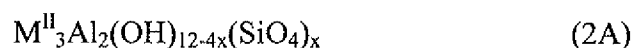


wherein M^{II} and M^{III} are as in formula (1) above, and y is in the range of about 0.05 to about 1.5, preferably in the range of about 0.1 to about 1.5, more preferably in the range of about 0.05 to about 1.2.

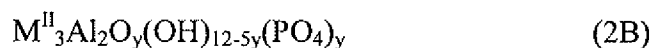
Another embodiment is synthetic hydrogarnets that may be represented by the following general empirical formula (2):



where M^{II} is a Group IIA metal atom, typically Ca, Sr, or Ba, or a mixture of at least two of these, or a mixture of any one or more of these with a minor proportion (*i.e.*, less than about 50% by weight) of Mg; and where x and y are numbers in the range of 0 to about 1.5, with $x + y$ in the range of about 0 to about 1.5, preferably in the range of about 0.05 to about 1.5; more preferably in the range of about 0.1 to about 1.5, even more preferably in the range of about 0.05 to about 1.2. Here again, the presence of trace amounts of other metal atoms that do not adversely affect the flame retardant and thermal stability properties of the flame retardant can be present. When no silicon or phosphorus source is used in synthesizing the product, the product can be represented by the formula $M^{II}_3Al_2(OH)_{12}$, where M^{II} is as in formula (2) above. When no phosphorus source is used in synthesizing the product, the synthetic hydrogarnet can be represented by the following general empirical formula:

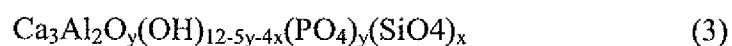


wherein M^{II} is as in formula (2) above, and x is in the range of about 0.05 to about 1.5, preferably in the range of about 0.1 to about 1.5, more preferably in the range of about 0.05 to about 1.2. When no silicon source is used in synthesizing the product, the synthetic hydrogarnet can be represented by the following general empirical formula:

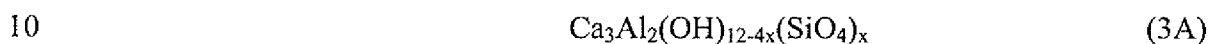


wherein M^{II} is as in formula (2) above, and y is in the range of about 0.05 to about 1.5, preferably in the range of about 0.1 to about 1.5, more preferably in the range of about 0.05 to about 1.2.

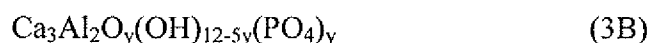
Another embodiment is a synthetic hydrogarnet represented by the following general empirical formula (3):



where x and y are numbers in the range of 0 to about 1.5, with x + y in the range of about 0 to about 1.5, preferably in the range of about 0.05 to about 1.5; more preferred ranges are about 0.1 to about 1.5 and about 0.05 to about 1.2. As above, the presence of trace amounts of other metal atoms that do not adversely affect the flame retardant and thermal stability properties of the flame retardant can be present. When no silicon or phosphorus source is used in synthesizing the product, the product can be represented by the formula $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$. When no phosphorus source is used in synthesizing the product, the synthetic hydrogarnet can be represented by the following general empirical formula:



wherein x is in the range of about 0.05 to about 1.5, preferably in the range of about 0.1 to about 1.5, more preferably in the range of about 0.05 to about 1.2. When no silicon source is used in synthesizing the product, the product can be represented by the following general empirical formula:



wherein y is in the range of about 0.05 to about 1.5, preferably in the range of about 0.1 to about 1.5, more preferably in the range of about 0.05 to about 1.2.

The synthetic hydrogarnets of this invention (synthetic hydrogarnets of formulas (1), (1A), (1B), (2), (2A), (2B), (3), (3A), or (3B) above) are flame retardants of increased effectiveness and are further characterized by having enhanced thermal stability. It is also believed that by virtue of the inclusion of silicate and/or phosphate in the crystal structure, the resultant crystal growth characteristics of the synthetic hydrogarnets can be influenced in a favorable manner. This in turn could have a beneficial influence on various characteristics of the synthetic hydrogarnets, such as purity. In this connection, in particularly preferred synthetic hydrogarnets of this invention (flame retardants of formulas (1), (1A), (1B), (2), (2A), (2B), (3), (3A), or (3B) above), at least about 98% by weight of M^{II} is Ca, and at least about 98% by weight of M^{III} is Al.

The process for producing the synthetic hydrogarnets may be found in WO 2010/059508, published on 27 May 2010. In general, the synthetic hydrogarnets may be produced by agitating a mixture formed from:

- (1) a Group IIIA metal source (especially an aluminum source),
- (2) a Group IIA metal source (especially an alkaline earth metal source),

- (3) optionally a source of silicon (especially an aqueous silicate solution, as for example, (i) one or more of the solutions of, *e.g.*, NaSiO_3 or $\text{Na}_2\text{Si}_3\text{O}_7$ such as are commercially-available as “water glass” and/or (ii) amorphous or crystalline silicon dioxide in powder form), and/or
- 5 (4) optionally a source of phosphorus (especially an aqueous phosphate solution, *e.g.*, phosphoric acid, alkali or ammonium phosphate salts such as Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4 , alkali or ammonium diphosphate salts such as $\text{Na}_4\text{P}_2\text{O}_7$, and/or alkali or ammonium polyphosphate salts),
- wherein said (1), (2), (3), and/or (4), independently, and/or their respective hydrates
- 10 are in solid form or in aqueous solution, and
- (5) an alkali metal hydroxide,
- and heating said agitated mixture at a temperature in the range of about 50 to about 100°C;
- optionally cooling the reaction product or allowing the reaction product to cool; and
- 15 recovering the resultant product;
- said process being further characterized in that the proportions of the Group IIIA metal source and the Group IIA metal source used in forming the mixture are in a molar ratio of Group IIA metal:Group IIIA metal in the range of about 1:1 to about 2:1. When present, the source of silicon used in forming the mixture provides silicate in amounts in the range of
- 20 about 0.05 to about 1.5 moles of silicate per mole of modified synthetic inorganic hydrogarnet prepared, and/or when present, the source of phosphorus used in forming the mixture provides phosphate in amounts in the range of about 0.05 to about 1.5 moles of phosphate per mole of modified synthetic inorganic hydrogarnet prepared. Preferred proportions of the source of silicon used in forming the mixture and/or the source of
- 25 phosphorus used in forming the mixture provide silicate and/or phosphate in amounts in the range of about 0.1 to about 1.5 moles, more preferably in the range of about 0.05 to about 1.2 moles, of silicate and/or phosphate per mole of modified synthetic inorganic hydrogarnet prepared. In general, each atom of silicon from the silicon source forms one silicate ion in the modified synthetic hydrogarnet, and each atom of phosphorus from the phosphorus
- 30 source forms one phosphate ion in the modified synthetic hydrogarnet.

A preferred process for producing the synthetic hydrogarnets of this invention relates to the incorporation therein of suitable amounts of silicate and/or phosphate. This process comprises:

agitating a mixture formed from a aluminum source, a calcium source, water, a source of silicon and/or phosphorus, and an alkali metal hydroxide, and heating said agitated mixture at a temperature in the range of about 50 to 100°C, the aluminum source being (i) aluminum hydroxide, boehmite, pseudo boehmite, aluminum oxide, or mixtures of any two or more of the foregoing, and (ii) in powder form, the calcium source being (i) an inorganic salt, hydroxide, or oxide of calcium, including hydrates thereof, and (ii) in powder form;

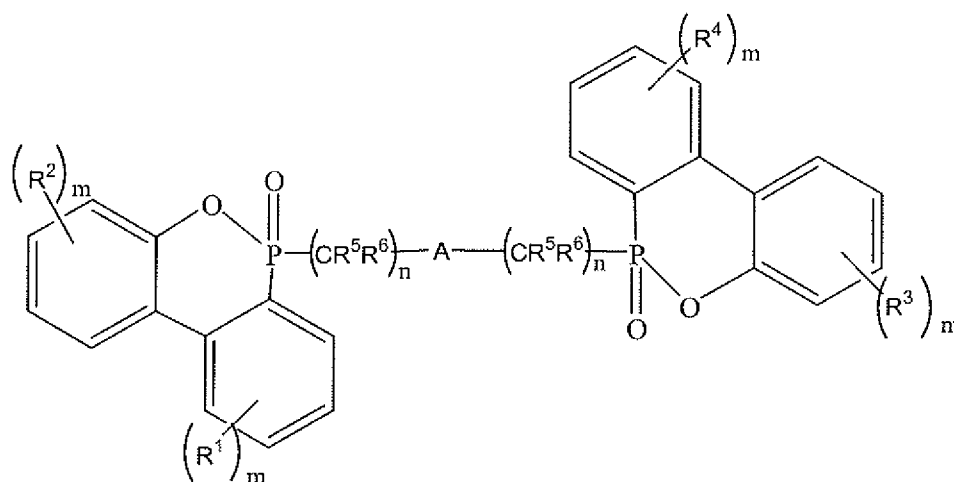
optionally cooling the reaction product or allowing the reaction product to cool; and recovering the resultant product;

10 said process being further characterized in that the proportions of aluminum source and calcium source used in forming the mixture provide a molar ratio of Ca:Al in the range of about 1:1 to about 2:1, and the source of silicon used in forming the mixture provides silicate in amounts in the range of about 0.05 to about 1.5 moles, preferably in the range of about 0.1 to about 1.5 moles, more preferably in the range of about 0.05 to about 1.2 moles, of silicate
15 per mole of synthetic flame retardant produced, and/or the source of phosphorus used in forming the mixture provides phosphate in amounts in the range of about 0.05 to about 1.5 moles, preferably in the range of about 0.1 to about 1.5 moles, more preferably about 0.05 to about 1.2 moles, of phosphate per mole of synthetic flame retardant produced.

As indicated above, a variety of raw materials can be utilized in preparing the
20 synthetic hydrogarnets of this invention. Non-limiting examples of Group IIA and IIA raw materials, and preferred embodiments and process conditions for producing the synthetic hydrogarnets may be found in WO 2010/059508.

Di-Dopo Compound

The application also provides a di-dopo compound having the following structure:



Formula I

wherein A is a direct bond, C₆-C₁₂ aryl, C₃-C₁₂ cycloalkyl, or a C₃-C₁₂ cycloalkenyl, wherein said cycloalkyl or cycloalkenyl may be optional substituted by a C₁-C₆ alkyl; each R¹, R², R³ and R⁴ are independently hydrogen, C₁-C₁₅ alkyl, C₆-C₁₂ aryl, C₇-C₁₅ aralkyl or C₇-C₁₅ alkaryl; or R¹ and R² or R³ and R⁴ taken together can form a saturated or unsaturated cyclic ring, wherein said saturated or unsaturated cyclic ring may be optional substituted by a C₁-C₆ alkyl; each m is independently 1, 2, 3 or 4; each R⁵ and R⁶ are independently hydrogen or a C₁-C₆ alkyl; and each n is independently 0, 1, 2, 3, 4 or 5; with the proviso that when A is aryl or a direct bond, n can not be 0.

In one aspect, both n subscripts are 1 or 2 and A is a direct bond. In another aspect, both n subscripts are 1 and A is a C₆-C₁₂ aryl. In another aspect, R¹, R², R³ and R⁴ are independently hydrogen or a C₁-C₆ alkyl. In another aspect, R⁵ and R⁶ are each independently hydrogen or methyl.

Specific compounds of Formula I that may be used in this invention are 6H-ibenz[c,e][1,2] oxaphosphorin, 6,6'-(1,2-ethanediyl)bis-, 6,6'-dioxide; 6H-Dibenz[c,e][1,2] oxaphosphorin, 6,6'-(1,4-butanediyl)bis-, 6,6'-dioxide; or 6H-Dibenz[c,e][1,2] oxaphosphorin, 6,6'-(*p*-xylenediyl)bis-, 6,6'-dioxide.

The term "alkyl", as used herein, unless otherwise indicated, includes saturated monovalent hydrocarbon radicals having straight or branched moieties. Examples of alkyl groups include, but are not limited to, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl and hexyl.

The term "aryl", as used herein, unless otherwise indicated, includes an organic radical derived from an aromatic hydrocarbon by removal of one hydrogen, such as phenyl, naphthyl, indenyl, and fluorenyl. "Aryl" encompasses fused ring groups wherein at least one ring is aromatic.

5 The term "aralkyl" as used herein indicates an "aryl-alkyl-" group. Non-limiting example of an aralkyl group is benzyl ($C_6H_5CH_2-$) and methylbenzyl ($CH_3C_6H_4CH_2-$).

The term "alkaryl" as used herein indicates an "alkyl-aryl-" group. Non-limiting examples of alkaryl are methylphenyl-, dimethylphenyl-, ethylphenyl-, propylphenyl-, isopropylphenyl-, butylphenyl-, isobutylphenyl- and t-butylphenyl-.

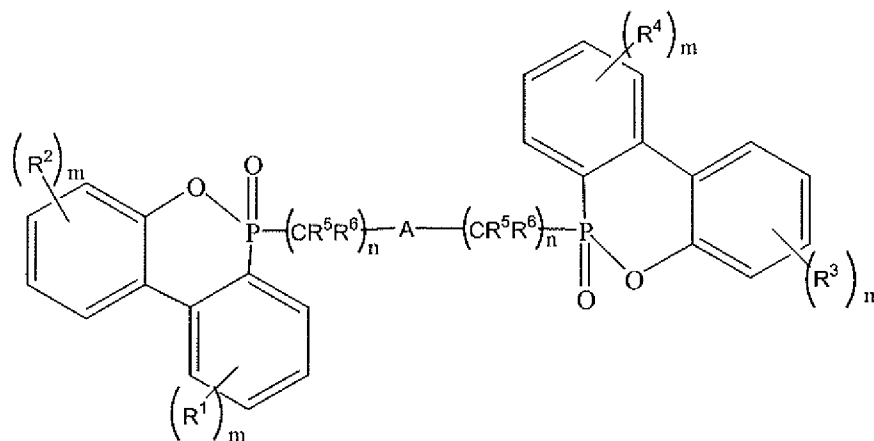
10 The term "alkenyl", as used herein, unless otherwise indicated, includes alkyl moieties having at least one carbon-carbon double bond wherein alkyl is as defined above. Examples of alkenyl include, but are not limited to, ethenyl and propenyl.

The term "cycloalkyl", as used herein, unless otherwise indicated, includes non-aromatic saturated cyclic alkyl moieties wherein alkyl is as defined above. Examples of
15 cycloalkyl include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and cycloheptyl.

The term "cycloalkenyl", as used herein, unless otherwise indicated, includes non-aromatic cyclic alkenyl moieties wherein alkenyl is as defined above. Examples of cycloalkyl
20 include, but are not limited to, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, and cycloheptenyl.

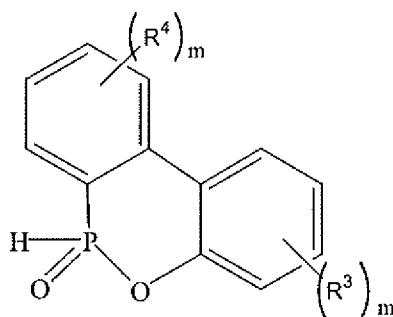
Unless otherwise indicated, all the foregoing groups derived from hydrocarbons may have up to about 1 to about 20 carbon atoms (e.g., C_1-C_{20} alkyl, C_6-C_{20} aryl, C_7-C_{20} alkaryl, C_7-C_{20} aralkyl) or 1 to about 12 carbon atoms (e.g., C_1-C_{12} alkyl, C_6-C_{12} aryl, C_7-C_{12} alkaryl, C_7-C_{12} aralkyl), or 1 to about 8 carbon atoms, or 1 to about 6 carbon atoms.

25 One process for making the di-dopo compounds of formula I may be found in PCT Applications PCT/US10/35359 and PCT/US10/35354. The process involves making the di-dopo compounds of formula I having the following structure:



Formula I

- 5 wherein A is a direct bond, C₆-C₁₂ aryl, C₃-C₁₂ cycloalkyl, or a C₃-C₁₂ cycloalkenyl, wherein said cycloalkyl or cycloalkenyl may be optional substituted by a C₁-C₆ alkyl; each R¹, R², R³ and R⁴ are independently hydrogen, C₁-C₁₅ alkyl, C₆-C₁₂ aryl, C₇-C₁₅ aralkyl or C₇-C₁₅ alkaryl; or R¹ and R² or R³ and R⁴ taken together can form a saturated or unsaturated cyclic ring, wherein said saturated or unsaturated cyclic ring may be optional substituted by a C₁-C₆
- 10 alkyl; each m is independently 1, 2, 3 or 4; each R⁵ and R⁶ are independently hydrogen or a C₁-C₆ alkyl; and each n is independently 0, 1, 2, 3, 4 or 5; with the proviso that when A is aryl or a direct bond, n can not be 0; comprising reacting a compound of Formula A:

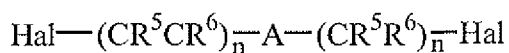


Formula A

15 wherein R³, R⁴ and m are defined above;

with a compound of Formula B in the presence of a base;

20



Formula B

5 wherein R^5 , R^6 and n are defined above and Hal is a halogen (e.g., F, Cl, I or Br); with the proviso that when A is aryl or a direct bond, n can not be 0.

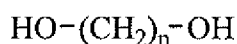
One base that may be used is an alkali metal base such as alkali metal alkoxides, alkali metal amides and alkali metal alkyl amides. Alkali metals for the base include lithium, sodium and potassium. Examples of the bases that may be used include, but are not limited
10 to, potassium methoxide, sodium methoxide, lithium methoxide, potassium ethoxide, sodium ethoxide, lithium ethoxide, potassium t-butoxide, sodium t-butoxide, lithium diisopropyl amide and mixtures thereof. Preferred are potassium t-butoxide and sodium methoxide.

Any suitable amount of base may be used in the process of this invention. Such suitable amounts include from about 0.1 to about 10 equivalence, or about 0.5 to about 5
15 equivalence, based on the amount of the compound of Formula A.

The process may also contain an optional solvent. Examples of such solvents may include, but are not limited to, heptane, hexane, petroleum ether, methylcyclohexane; toluene, xylene, ethyl benzene, tetrahydrofuran, dimethyl sulfoxide (DMSO), 1,4-dioxane, dimethyl formamide (DMF), dimethylacetamide (DMAc), acetonitrile, ethylene glycol, dimethyl ether,
20 ethylene glycol diethyl ether or mixtures thereof.

The process may be conducted at temperatures ranging from about -10°C to about 75°C .

Another process that may be used to produce an alkylene bridge compounds of Formula I may be found in U.S. Provisional Application Nos. 61/319580 and 61/410,694
25 filed on March 31, 2010 and November 5, 2010 respectively, both entitled Process for the Preparation of DOPO-Derived Compounds, both herein incorporated by reference in their entirety. In that process, DOPO is reacted with a compound of Formula C:



30

Formula C

in the presence of a catalyst at temperatures ranging from about 100°C to about 250°C . The catalyst that may be used is any suitable catalyst for dehydration and/or Arbuzov reactions.
35 General suitable catalysts are, alky halides, alkali halides, alkaline earth metal halides, transition metals and their halides or acid catalysts such as methyl p-toluenesulfonate, ethyl

p-toluenesulfonate. Arbuzov reaction catalysts are especially suitable. The process may optionally use a solvent, preferably a high boiling point solvent and an optional entrainer.

It is preferred that the purity of the compounds of Formula I, when combined with epoxies should be greater than about 95%, or about 98% or about 99%. The purity levels can be measured by using NMR spectroscopy. One skilled in the art of NMR spectroscopy can develop a procedure for measuring the purity of the compound of Formula I and one procedure may be found in PCT/US10/35359.

Preferably, the compound of formula I is grounded or milled prior to combining with the polymer. The d_{50} particle size after grinding or milling may be less than about 15 μm , or less than 10 μm , or less than about 5 μm , or less than about 3 μm or less than about 2 μm . The d_{50} particle size may even be less than 1 μm , such as about 100 nm to 800 nm. A particle size of d_{50} is the median particle size, where half the particles are above the value and half the particles are below the value. Any suitable milling or grinding technique may be used such as jet milling.

It is also preferred that the compound of Formula I have a monomodal particle size distribution, preferably when the d_{50} particle size is greater than about 2 μm so that the compound may be more homogeneously blended with the polymer.

To determine median particle size, a Coulter LS-230 counter or equivalent is used with its small volume module. The operating instructions of the manufacturer are followed. Alternatively, a Horiba laser light scattering instrument (*e.g.*, Horiba LA900 Model 7991) or equivalent can be used. The procedure involves weighing the sample, typically an amount in the range of about 0.01 gram to about 0.015 gram, into a clean dry aluminum cup that has been washed with deionized water before use. The instrument autosampler disperses a 0.05 g sample in water using 0.4 mL of 1% Triton X-100 surfactant and ultrasonic treatment. This suspension is circulated through a measuring cell where the powder particles scatter a beam of laser light. Detectors in the instrument measure intensity of the light scattered. The computer in the instrument calculates mean particle size, average particle size and particle size distribution from such measurements.

It is preferred that the compound of Formula I is substantially or completely free of organic bases because organic bases may deleteriously affect its use as a flame retardant, especially when used in epoxies. Substantially free of organic bases means that the levels are less than about 10,000 ppm, or less than about 1000 ppm, or less than about 100 ppm or less than about 10 ppm. One method to have the compound of Formula I be substantially or completely free of an organic base is not to use the any organic base in the reaction to

produce the compound. One method to determine the amount of organic base, if any, is NMR spectroscopy.

An organic base is an organic compound, which acts as a base. Organic bases are usually, but not always, proton acceptors. They usually contain nitrogen atoms, which can be readily protonated. Amines and nitrogen-containing heterocyclic compounds are typically organic bases. Examples include, but are not limited to pyridine, methyl amine, trimethylamine, triethylamine, tripropylamine, tributylamine, N-ethylmorpholine, imidazole, benzimidazole, histidine, phosphazene bases and carbonates or hydroxides of some organic cations.

It is preferred that the compound of Formula I is substantially free of unreacted DOPO because DOPO may deleteriously affect its use as a flame retardant. Substantially free of DOPO means that the levels are less than about 50,000 ppm, or less than about 20,000 ppm, or less than about 10,000 ppm or less than about 1000 ppm or less than about 100 ppm. A preferred method to reduce the DOPO is to wash the product with water or water miscible solvents such as alcohols (e.g., isopropanol), aldehydes or ketones (e.g., acetone) before and/or after filtration. DOPO levels may be measured by using NMR spectroscopy.

It is preferred that the amount of solvent remaining in the compound of Formula I after purification should be less than about 1000 ppm, or less than about 100 ppm, or less than about 50 ppm. The amount of solvent may be measured by using NMR spectroscopy.

One method to reduce the amount of solvent in the compound of Formula I is drying under vacuum or with nitrogen sweep at temperature from about 100°C to 170°C for about 2 to about 24 hours. If the compound is grounded or milled, it is preferred to do at temperatures above room temperature, such as by hot air jet milling to further reduce volatiles.

Epoxy Resin

Any suitable epoxy resin useful in the art may be used in the present invention as the epoxy compound. Representative epoxy resins suitable for use in the present invention are presented in Epoxy Resins Chemistry and Technology, Second Edition edited by Clayton A. May (Marcel Dekker, Inc. New York, 1988), Chemistry and Technology of Epoxy Resins edited by B. Ellis (Blackie Academic & Professional, Glasgow, 1993), Handbook of Epoxy Resins by H. E. Lee and K. Neville (McGraw Hill, New York, 1967).

It is generally advantageous to use an epoxy resin, which possesses an average functionality more than 1 and preferably at least 1.8, more preferably at least 2 epoxy groups

per molecule. In the more preferred case, the epoxy resin is a novolac epoxy resin with at least 2.5 epoxy groups per molecule. In another aspect of the invention, the epoxy resin may be any saturated or unsaturated aliphatic, cycloaliphatic, aromatic or heterocyclic compound, which possesses more than one 1,2-epoxy groups. Examples of heterocyclic epoxy
5 compounds are diglycidylhydantoin or triglycidyl isocyanurate (TGIC).

Suitable epoxy resins are, but not limited to, epoxy resins based on bisphenols and polyphenols, such as, bisphenol A, tetramethylbisphenol A, bisphenol F, bisphenol S, tetrakisphenylolethane, polybenzoxazine, resorcinol, 4,4'-biphenyl, dihydroxynaphthylene, and epoxy resins derived from novolacs, such as, phenol:formaldehyde novolac,
10 cresol:formaldehyde novolac, bisphenol A novolac, biphenyl-, toluene-, xylene, or mesitylene-modified phenol:formaldehyde novolac, aminotriazine novolac resins and heterocyclic epoxy resins derived from p-amino phenol and cyanuric acid. Additionally, aliphatic epoxy resins derived from 1,4-butanediol, glycerol, and dicyclopentadiene skeletons, are suitable, for example. Many other suitable epoxy resin systems are available
15 and would also be recognized as being suitable by one skilled in the art.

Epoxy novolac resins (including epoxy cresol novolac resins) are readily commercially available, for example, under the trade names D.E.N.TM, QUATREX.TM (Trademarks of the Dow Chemical Company), TactixTM 742 (Trademarks of Ciba) and EponTM (trademark of Resolution Performance Products). The materials of commerce
20 generally comprise mixtures of various glycidoxyphenyl and methyl-, ethyl- propyl-glycidoxyphenyl groups.

In general, the amount of the compound of Formula I in the flame retardant epoxy composition is about 0.1 to about 100 parts, or about 1 to 70 parts, by weight per 100 parts by weight of the epoxy compound.

Alternatively, the amount of the phosphorus compound of Formula I in the flame retardant epoxy composition is selected so the composition will contain about 0.5 wt% to about 10 wt % or about 1.2 wt% to about 7 wt%, or about 1.5 wt% to about 5 wt% phosphorous content, based on the total weight of the composition.

In general, the amount of the synthetic hydrogarnet in the flame retardant epoxy
30 composition is about 0.1 to about 100 parts, or about 1 to 70 parts, by weight per 100 parts by weight of the epoxy compound.

The phosphorus-containing flame retardant epoxy composition has an epoxy equivalence of generally about 100 g/eq to about 1000 g/eq., or about 100 g/eq to about 800 g/eq or about 150 g/eq to about 500 g/eq.

Dispersants or wetting agents may also be used in the flame retardant epoxy composition. Dispersant are compounds that are used to suspend or disperse particles in a liquid medium and are usually polymer or oligomeric in nature. A discussion of dispersants may be found in Kiri-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons, 5 Vol. 8, page 672-697, 5th edition 2004. Any suitable dispersant may be used in the flame retardant epoxy composition.

Non-limiting examples of suitable dispersants are alkylammonium salts of a polycarboxylic acid; alkylammoniums salt of a fatty acid; alkanolammonium salts of an acidic polymer; propylene glycol methyl ether acetate or polyethylene glycol monomethyl 10 ether both optionally containing small amounts of polyphosphoric acids or polyphosphate oligomers; or mixtures thereof.

In one embodiment, the alkylammonium salt of a polycarboxylic acid may be represented by the following formula:



wherein each R^{11} is independently a $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_3\text{-C}_{18}$ cycloalkyl, $\text{C}_6\text{-C}_{18}$ aryl or a $\text{C}_7\text{-C}_{18}$ aralkyl; R^{12} is a $\text{C}_1\text{-C}_{100}$ hydrocarbylene group, optionally containing ether linkages, and n is 1 to about 50. These types of quaternary alkylammonium polycarboxylic acid compounds 20 are well known in the art. For example, U.S. Patent No. 5,891,921, herein incorporated by reference, discloses many such alkylammonium polycarboxylic acid compounds and how they are prepared. Polycarboxylic acids may be converted into quaternary ammonium salts either through neutralization with a quaternary ammonium hydroxide or through anion exchange with a quaternary ammonium carbonate.

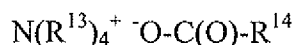
25 In one embodiment, R^{11} is a $\text{C}_1\text{-C}_{18}$ alkyl. In another embodiment, R^{12} is $\text{C}_2\text{-C}_{20}$ alkylene. In another embodiment, n is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

Examples of suitable quaternary ammonium cations include tetraalkyl(C_{1-18}) ammoniums, such as trimethylethyl-, triethylmethyl-, trimethylhexyl-, trimethyloctyl-, tributyl-octyl-, trimethyldecyl-, trimethyltetradecyl-, trimethylcetyl- and methyltrioctyl- 30 ammoniums. Examples of the polycarboxylic acids that may be used to form the anion include, but are not limited to anions of polycarboxylic acid derived from: oxalic acid, malonic acid, succinic acid glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid, tetradecanedioic acid, pentadecanedioic acid, hexadecanedioic acid, heptadecanedioic acid, octadecanedioic acid, 35 nonadecanedioic acid, eicocanedioic acid, phthalic acid, isophthalic acid, terephthalic

acid, hexahydrophthalic acid, citric acid, aconitic acid, propane-1,2,3-tricarboxylic acid, trimesic acid or mixtures thereof.

Another dispersant, which is used in the present invention, is an alkylammonium salt of a fatty acid. It may be represented by the following formula:

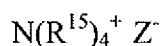
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wherein each R^{13} is independently a $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_3\text{-C}_{18}$ cycloalkyl, $\text{C}_6\text{-C}_{18}$ aryl or a $\text{C}_7\text{-C}_{18}$ aralkyl; R^{14} is a $\text{C}_1\text{-C}_{30}$ alkyl, or $\text{C}_1\text{-C}_{30}$ alkenyl.

10 Fatty acids may be converted into quaternary ammonium salts either through neutralization with a quaternary ammonium hydroxide or through anion exchange with a quaternary ammonium carbonate. In one embodiment, the fatty acid anion is derived from unsaturated fatty acids. Examples of such unsaturated fatty acids, include, but are not limited to: myristoleic acid, palmitoleic acid, oleic acid, linoleic acid, α -linolenic acid, arachidonic
15 acid, eicosapentaenoic acid, erucic acid, docosahexaenoic acid or mixtures thereof. Examples of suitable quaternary ammonium cations include, but are not limited to tetraalkyl($\text{C}_1\text{-C}_{18}$) ammoniums, such as trimethylethyl-, triethylmethyl-, trimethylhexyl-, trimethyloctyl-, tributyl-octyl-, trimethyldecyl-, trimethyltetradecyl-, trimethylcetyl- and methyltrioctyl-ammoniums.

20 Another dispersant, which is used in the present invention, is an alkanolammonium salt of an acidic polymer. It may be represented by the following formula:



25 wherein each R^{15} is independently a $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_3\text{-C}_{18}$ cycloalkyl, $\text{C}_6\text{-C}_{18}$ aryl, $\text{C}_7\text{-C}_{18}$ aralkyl, $\text{C}_1\text{-C}_{15}$ hydroxyalkyl, $\text{C}_3\text{-C}_{18}$ hydroxycycloalkyl $\text{C}_6\text{-C}_{18}$ hydroxyaryl or a $\text{C}_7\text{-C}_{18}$ hydroxyaralkyl; provided that at least one R^{15} contains a hydroxy group; Z is a carboxyl-containing polymer having a number average molecular weight (Mn) of 1000 to 100,000.

Alkanolammonium salt of an acidic polymer are known in the art. For example, U.S.
30 Patent No. 6,680,266, herein incorporated by reference, discloses many such alkylammonium acidic polymer compounds and how they are prepared. Carboxyl-containing polymers may be converted into quaternary ammonium salts either through neutralization with a quaternary ammonium hydroxide or through anion exchange with a quaternary ammonium carbonate.

Suitable examples of R^{15} hydroxyalkyl groups, include, but are not limited to:
35 hydroxyethyl, hydroxypropyl, hydroxybutyl, hydroxyhexyl and hydroxyoctyl.

Suitable examples of quaternary alkanolammonium cations that may be used, include, but are not limited to: trihydroxyalkyl(C₂-C₈) alkyl(C₁-C₆) ammoniums, such as trihydroxyethylhexyl ammonium; trihydroxymethylethyl ammonium; trihydroxy ethylpentyl ammonium; trihydroxymethylbutyl ammonium; stearyltrihydroxyethyl ammonium; 5 dialkyl(C₈-C₁₈)dihydroxyethylammonium salts such as dilauryldihydroxy ethylammonium.

The carboxyl-containing polymers have an Mn of about 1,000 to about 100,000, or about 3,000 to about 30,000 and an Mw of generally about 1,100 to about 150,000, or about 3,300 to about 40,000. The polymers have an acid value of usually at least about 250, or about 500 to about 970, or about 550 to about 900, or about 700 to about 780.

10 One embodiment of an acidic polymer is an ethylenically unsaturated carboxyl-containing monomer or a copolymer of an ethylenically unsaturated carboxyl-containing monomer with at least one other polymerizable monomer. Suitable ethylenically unsaturated carboxyl-containing monomers include, but are not limited to α,β -unsaturated monocarboxylic acids, such as (meth)acrylic and crotonic acids; dicarboxylic acids, such as 15 maleic, fumaric, itaconic, citraconic, mesaconic, methylenemalonic and cinnamic acids, tricarboxylic acids, such as aconitic acid; dicarboxylic anhydrides, such as maleic, itaconic and citraconic anhydrides; half esters of dicarboxylic acid as mentioned above with monohydric alcohol (e.g. alkanols, cellosolves and carbitols, containing 2 to 16 carbon atoms), such as monobutyl maleate, monoethylcarbitol maleate and the like, fumarates and 20 itaconates corresponding to these maleates; as well as combinations of two or more of these monomers.

Another embodiment of an acidic polymer is a carboxyl-containing polyester. Such resins are derived from the reaction of a dicarboxylic acid or anhydride with a polyhydric compound. Polycarboxylic acids such as phthalic acid, maleic acid, fumaric acid, isophthalic 25 acid, terephthalic acid, hexahydrophthalic acid, succinic acid, dodecylsuccinic acid, nadic acid, adipic acid, azelaic acid, sebacic acid, dimer acid, as well as anhydrides of such acids where they exist are useful. Preferred are phthalic acid, isophthalic acid, terephthalic acid, hexahydrophthalic acid, succinic acid, dodecylsuccinic acid, maleic acid, nadic acid, their anhydrides where they exist, and mixtures thereof. Polyhydric alcohols which are reacted 30 with the polycarboxylic acid or anhydride include glycerol, trimethylolethane, trimethylolpropane, pentaerythritol, sorbitol, mannitol, ethylene glycol, diethylene glycol, 2,3-butylene glycol and oxyalkylated derivatives thereof. Preferred are pentaerythritol, trimethylolpropane, glycerol, oxyalkylated derivatives and mixtures thereof. Molar ratios of the two reactants are selected so that the resultant polyester resin is carboxyl rich.

Commercial examples of such dispersant are the line of dispersants and wetting agents are typically available from suppliers such as Avecia Additives and BYK Chemie, such as Byk® W903, W935, W961, and W969. The choice of a particular type of surfactant, wetting agent or dispersant depends upon the resin and the desired properties of the laminate or printed wiring board.

While the amounts of the dispersant or wetting agent can vary, typically the amount on a weight basis added to the composition is in the range of about 0.01wt% to about 4wt% or in the range of about 0.1wt% to about 2wt%, based on the total weight of the composition.

The synthetic hydrogarnets may also be at least partially coated with a silane coating agent. Examples of such silanes that may be used are: aminopropyltriethoxysilane, aminoethylaminopropyltrimethoxysilane, aminoethylaminopropyltrimethoxysilane, aminoethylaminopropylsilane, 3-aminopropyltrimethoxysilane, N-(2-aminoethyle)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-cyclohexyl-3-aminopropyltrimethoxysilane, benzylaminoethylaminopropyltrimethoxysilane, vinylbenzylaminoethylaminopropyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyl dimethoxymethylsilane, vinyl(tris)methoxyethoxy)silane, vinylmethoxymethylsilane, vinyltris(2-methoxyethoxy)silane, vinyltriacetoxysilane, methyltrimethoxysilane, n-hexyltrimethoxysilane, n-octyltriethoxysilane, propyltrimethoxysilane, propyltriethoxysilane, t-butyltrimethoxysilane, isobutyltriethoxysilane, chloropropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, glycidoxypropylmethyldiethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, mercaptopropyltrimethoxysilane, bis-triethoxysilylpropyldisulfidosilane, bis-triethoxysilylpropyldisulfidosilane, bis-triethoxysilylpropyltetraasulfidosilane, tetraethoxysilane, N-cyclohexylaminomethylmethyldiethoxysilane, n-cyclohexylaminomethyltriethoxysilane, n-phenylaminomethyltrimethoxysilane, (methacryloxymethyl)methyldimethoxysilane, methacryl-oxymethyltrimethoxysilane, (methacryloxymethyl)methyldiethoxysilane, methacryloxymethyl-triethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltriacetoxysilane, (isocyanatomethyl)methyldimethoxysilane, 3-isocyanatopropyltrimethoxysilane, 3-trimethoxysilylmethyl-O-methylcarbamate, n-dimethoxy-(methyl)silylmethyl-O-methylcarbamate, 3-(triethoxysilyl)propyl succinic anhydride, methyltrimethoxysilane, methyltriethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, trimethylethoxysilane, isoctyltrimethoxysilane, isoctyltriethoxysilane,

hexadecyltrimethoxysilan, (octadecyl)methyldimethoxysilane, phenyltriethoxysilane, (cyclohexyl)methyldimethoxysilane, dicyclopentyl dimethoxysilane and tetraethylsilicate.

The synthetic hydrogarnets may be coated with the silane by any suitable method. One method is spray coating, where the silane is sprayed on well agitated synthetic hydrogarnets using mixing equipment from manufactures such as such Loedige, Littleford
5 Day, Hosokawa Alpine, and Thyssen Henschel.

Example of commercial silanes that may be used are the line of multifunctional silanes Dynasytan® from Degussa (Evonik Industries AG).

The present invention also relates to a cured flamed retardant epoxy resin comprising
10 the flame-retardant epoxy resin composition above reacted with a curing or polymer initiation agent.

The aforementioned curing or polymerization initializing agents are not limited to a specific curing or polymerization initializing agent as long as the agent helps polymerization of the epoxy resin in the flame retardant epoxy composition.

15 Examples of polymerization initializing agents are cationic polymerization initializing agents such as methane sulfonic acid, aluminum chloride, stannum chloride, trifluoroboron ethylamine complex, trifluoroboron ethylether complex and the like; radical polymerization initializing agents such as benzoyl peroxide, dicumyl peroxide, azo bis-isobutyronitrile and the like; and anionic polymerization initializing agents such as methoxy potassium, triethyl
20 amine, 2-dimethyl aminophenol and the like and mixtures thereof.

The aforementioned epoxy curing agents include any agent known by a person skilled in the art. Examples, include but are not limited to: ethylene diamine, trimethylene diamine, tetramethylene diamine, hexamethylene diamine, meta phenylene diamine, para phenylene diamine, para xylene diamine, 4,4'-diamino diphenyl methane, 4,4'-diamino diphenyl
25 propane, 4,4'-diamino diphenyl ether, 4,4'-diamino diphenyl sulfone, 4,4'-diamino dicyclohexane, bis (4-aminophenyl) phenyl methane, 1,5-diamino naphthalene, meta xylylene diamine, para xylylene diamine, 1,1-bis (4-aminophenyl) cyclohexane, dicyan diamide, phenol/formaldehyde novolac, cresol/formaldehyde novolac, bisphenol A novolac, biphenyl-, toluene-, xylene-, or mesitylene-modified phenol/formaldehyde novolac, aminotriazine
30 novolac, cresol/formaldehyde/aminotriazine novolac, phenol/formaldehyde/aminotriazine novolac or mixtures thereof.

The amount of curing agent that may be used is based on the molar equivalence of curing functional groups in the curing agent to the molar equivalence of un-reacted epoxy groups in the flame-retardant epoxy resin composition. Thus, the curing agent amount may

be from about 0.1 equivalence to about 10 equivalence or about 0.3 equivalence to about 5 equivalence, or about 0.7 equivalence to about 2 equivalence based on the equivalence of unreacted epoxy groups in the phosphorus-containing epoxy resin.

The polymerization initializing agents may be added in concentrations ranging from
5 about 0.01 wt% to about 10 wt %, or about 0.05 to about 5%, or about 0.1 wt% to about 2 wt%, based on the total weight of the flame-retardant epoxy resin composition.

The curing temperature may be carried out generally between about 25°C to about 250°C, or about 70°C to about 240°C or about 150°C to about 220°C.

In addition, epoxy curing agent promoters may also be used to promote curing of the
10 flame retardant epoxy composition. These epoxy curing agent promoter are often based on imidazoles. Examples of such epoxy curing agent promoters include, but are not limited to: 1-methylimidazole, 2-methylimidazole, 1,2-dimethylimidazole, 1,2,4,5-tetramethylimidazole, 2-ethyl-4-methylimidazole, 2-phenylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-(4,6-diamino-s-triazinyl-2-ethyl)-2-phenylimidazole or mixtures thereof.

15 When phenol novolacs are used as curing agents, the epoxy curing agent promoter may be added in concentrations ranging from about 0.0001 wt% to about 5 wt %, or about 0.01 to about 3%, or about 0.1 wt% to about 2 wt%, or about 0.15 wt% to about 1 wt%, based on the weight of curing agent used. Higher concentrations of promoter may be used with different curing agents, such as DICY, dicyandiamide, where promoter concentrations are
20 more typically in the 5-25 wt% range, based on weight of curing agent.

The aforementioned cured flamed retardant epoxy resin and/or flame-retardant epoxy compositions of the invention may also contain other conventional additives, such as heat stabilizers, light stabilizers, ultra-violet light absorbers, anti-oxidants, anti-static agents, preservatives, adhesion promoters, coupling agents such as amino-, vinyl- or alkyl silanes or
25 maleic acid grafted polymers; sodium stearate or calcium stearate, ; metal scavengers or deactivators fillers, pigments, dyes, lubricants, mold releasers, blowing agents, fungicides, plasticizers, processing aids, acid scavengers, dyes, pigments, nucleating agents, wetting agents, dispersing agents, synergists, mineral fillers, reinforcing agents such as glass fiber, glass flake, carbon fiber, or metal fiber; whiskers such as potassium titanate, aluminum
30 borate, or calcium silicate; inorganic fillers and other fire-retardant additives and smoke suppressants and mixtures thereof.

The other fire retardant additives, which may be used, include, but are not limited to, ammonium polyphosphate, nitrogen-containing synergists such as melamine polyphosphate, antimony oxide, silica, hydrated alumina such as aluminum hydroxide (ATH), boehmite,

bismuth oxide, molybdenum oxide, or mixtures of these compounds with zinc, aluminum and/or magnesium oxide or salts.

Inorganic fillers may be used in the invention to affect physical properties and to reduce costs. Typically, fillers and reinforcing agents include fused silica powder; crystalline silica powder; alumina; silicon nitride; aluminum nitride; boron nitride; magnesia; titanium oxide; calcium carbonate; magnesium carbonate; calcium silicate; glass fiber; asbestos, talc, kaolin, bentonite, wollastonite, glass fiber, glass fabrics, glass matt, milled glass fiber, glass beads (solid or hollow), silicon carbide whiskers and mixtures thereof. Many of these materials are enumerated in the Encyclopedia of Materials Science and Engineering, Vol. # 3, pp. 1745 1759, MIT Press, Cambridge, Mass. (1986), the disclosure of which is incorporated herein by reference. Combinations of fillers are preferred in some embodiments; whereas in other embodiments, the reinforcing agent makes up much of the composite of the invention, as in the case of glass fabric used in prepregs and laminates for printed wiring boards.

Other flame retardants or combinations of different other flame retardants can be added to the flame retardant composition. Non limiting examples of these additional flame retardants are mineral flame retardants like aluminum hydroxides, magnesium hydroxides, boehmites, layered double hydroxides (LDH), organically modified LDHs, clays, organically modified nano-clays, zinc borates, zinc stannates and zinc hydroxy stannates, brominated flame retardants, phosphorus containing flame retardants, nitrogen containing flame retardants and the like.

The aforementioned cured flamed retardant epoxy resin and/or flame-retardant epoxy composition of the invention may be used to form prepreg and/or laminates. Typical procedures for forming prepregs and laminates for printed wiring boards involve such operations as:

- A) An epoxy-containing formulation such as one containing the flame retardant epoxy composition of the present invention is formulated with solvents and curing or polymerization agents and optionally other conventional additives described above. The formulation is applied to or impregnated into a substrate by rolling, dipping, spraying, other known techniques and/or combinations thereof. The substrate is an inorganic or organic reinforcing agent in the form of fibers, fleece, fabric, or textile material, *e.g.*, typically a woven or non-woven fiber mat containing, for instance, glass fibers or paper.
- B) The impregnated substrate is "B-staged" by heating at a temperature sufficient to draw off solvent in the epoxy formulation and optionally to partially cure the epoxy

formulation, so that the impregnated substrate cooled to room temperature is dry to the touch and can be handled easily. The "B-staging" step is usually carried out at a temperature of from 90°C to 240°C and for a time of from 1 minute to 15 minutes. The impregnated substrate that results from B-staging is called a "prepreg." The temperature is most commonly 100°C for composites and 130°C to 200°C for electrical laminates.

- 5
- C) One or more sheets of prepreg are stacked or laid up in alternating layers with one or more sheets of a conductive material, such as copper foil, if an electrical laminate is desired.
- 10 D) The laid-up sheets are pressed at high temperature and pressure for a time sufficient to cure the resin and form a laminate. The temperature of this lamination step is usually between 100°C and 240°C, and is most often between 165°C and 200°C. The lamination step may also be carried out in two or more stages, such as a first stage between 100°C and 150°C and a second stage at between 165°C and 200°C. The pressure is usually between 50 N/cm² and 500 N/cm². The lamination step is usually carried out for a time of from 1 minute to 200 minutes, and most often for 45 minutes to 120 minutes. The lamination step may optionally be carried out at higher temperatures for shorter times (such as in continuous lamination processes) or for longer times at lower temperatures (such as in low energy press processes).
- 15
- E) Optionally, the resulting laminate, for example, a copper-clad laminate, may be post-treated by heating for a time at high temperature and ambient pressure. The temperature of post-treatment is usually between 120°C and 250°C. The post-treatment usually is between 30 minutes and 12 hours.
- 20
- F) Often an electrically-conductive printed circuit is applied to the copper-clad laminate. Typically, the solvent for the epoxy resin in step A above is a ketone such as 2-butanone or methyl ethyl ketone (MEK). However, any other suitable type of conventionally-used solvent for forming these formulations can be employed. Examples of such other solvents include, but are not limited to acetone, methyl isobutyl ketone (MIBK), 2-methoxy ethanol, 1-methoxy-2-propanol, propylene glycol monomethyl ether, ethylene glycol monoethyl ether acetate, toluene, N,N-dimethylformamide, and mixtures thereof.
- 25
- 30

EXAMPLES

The following Examples illustrate the present invention. It is to be understood, however, that the invention, as fully described herein and as recited in the Claims, is not intended to be limited by the details of the following Examples.

EXAMPLE 1

Synthetic hydrogarnet (Ca₃Al₂(OH)_{10.8}(SiO₄)_{0.3})

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In this Example, the initial charges to the 20-liter vessel were 4 liters of water, followed by 4 kg Solvay liquor with NaOH conc. of 50 wt.%, 11.7 kg of a 20% solids slurry of unmilled Ca(OH)₂ and 680 g of water glass (Na₂Si₃O₇) sodium silicate solution, having a calculated SiO₂ concentration of 27 wt% (available from Riedel-de Haën). This mixture was heated while stirring to 95°C at a rate of about 15°C per minute. At reaching the desired temperature, 1850 grams of fine precipitated aluminum trihydrate were added. This provides a theoretical amount of silicate equivalent to 0.3 mole per mole of synthetic flame retardant, giving the product Ca₃Al₂(OH)_{10.8}(SiO₄)_{0.3}. The mixture was maintained at this temperature, while stirring, for one hour. The product was then recovered, washed in a filter press and dried in a spray drier. The product had a d₅₀ particle size of about 3.5 μm.

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EXAMPLE 2

Synthetic hydrogarnet (Ca₃Al₂(OH)_{10.8}(SiO₄)_{0.3})

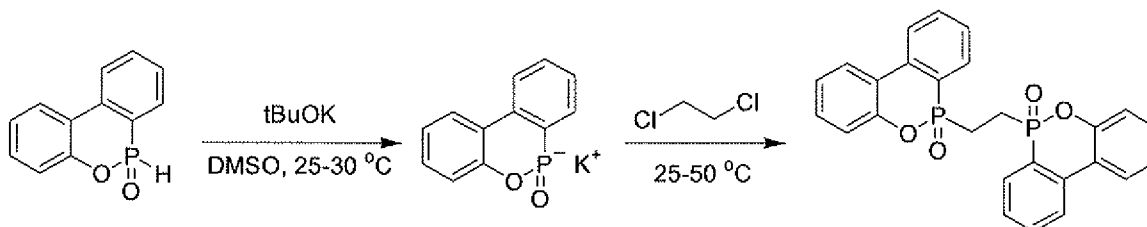
25

The procedure in Example 1 above was followed except that the Ca(OH)₂ was milled prior to combining with the other components. The d₅₀ of the final product was about 1.1 μm.

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EXAMPLE 3

6H-Dibenz[c,e][1,2]oxaphosphorin, 6,6'-(1,2-ethanediyl)bis-, 6,6'-dioxide



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TABLE 1. PREPARATION OF DIDOPO COMPOUND OF EXAMPLE 3

Component	MW (g/mol)	m.p (°C)	b.p (°C)	Physical state	moles	grams	mls	Eq.
DOPO, CAS # 35948-25-5 TCI America	216.17	119	-	Solid	1.96	423	-	2.1
<i>t</i> BuOK, CAS # 865-47-4, Sigma-Aldrich, St. Louis, MO	112.21	256-258	-	Solid	2.05	230	-	2.2
DMSO, CAS # 67-68-5, Sigma-Aldrich, St. Louis, MO	78.13	16-19	189	Liquid	21.12	1650	1500	12
Dichloroethane CAS # 75-34-3, Sigma-Aldrich, St. Louis, MO	98.96	-35	83	Liquid	0.93	92	73	1.0

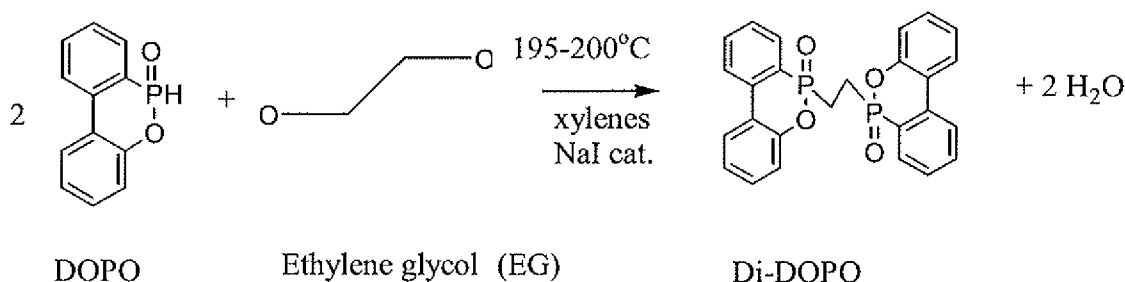
5 A 4-neck 5L half-jacketed reactor was fitted with an addition funnel, thermocouple, mechanical stirrer and nitrogen flow. The reactor was charged with potassium *t*-butoxide (*t*BuOK) (230 g, 2.05 mol) and 1.5 L of anhydrous DMSO as solvent. The mixture was stirred at room temperature until it became a homogenous solution. The solution was cooled to 10°C, and DOPO (423 g, 1.96 mol) was added in nine small portions, keeping the reaction

10 temperature below 30 °C (50-60 g per portion). Dichloroethane (92 g, 0.93 mol) in a 125 ml addition funnel was added to the above solution slowly during 1h. The reaction was heated to 50 °C for 1h. The reaction was cooled to 10 °C, and water (3 L) was added. The slurry was filtered, and the wet cake was washed with water, acetone and ethyl acetate to give 532 g of crude wet material. The crude material was refluxed in MeCN/ethanol/H₂O (5320 ml, v:v:v

15 = 1:1:0.5) and cooled to 5 °C slowly. The white solid was filtered through a coarse fritted funnel and dried in a vacuum oven for 8 h at 80 °C to afford a dry white powder (260 g, 68 wt% yield, 99.4 wt% purity, 253-269 °C m.p.). ³¹P-NMR(162 MHz, CDCl₃): δ 36.45, 36.25 ppm and ¹H-NMR (400MHz, CDCl₃): δ 7.95 (d, J = 8 Hz, 2H, ArH), 7.88 (d, J = 8 Hz, 2H, ArH), 7.79-7.69 (m, 4H, ArH), 7.48 (dd, J = 7.2 Hz, 14.4 Hz, 2H), 7.37 (dd, J = 7.2 Hz, 7.2

20 Hz, 2H, ArH), 7.29-7.24 (m, 2H, ArH), 7.16 (d, J = 12 Hz, 2H, ArH), 2.31 (m, 4H) ppm.

EXAMPLE 4

6H-Dibenz[c,e][1,2]oxaphosphorin, 6,6'-(1,2-ethanediyl)bis-, 6,6'-dioxide

High purity DOPO was loaded into a reactor and a given amount of mixed xylenes was then pumped into the reactor. A 2.62 wt% NaI/EG solution was prepared and charged to the reactor. The were then agitated and heated to 198°C in 5-6 hours while the pressure was maintained at 40-41 psig. Once the contents reached the reaction temperature, a co-feed containing the 2.62 wt% NaI/EG and mixed xylenes was started. The co-feed lasted a minimum of about 14 hours.

The xylene feed rate was on the order of 1lb/min. After an 11.5-hour feed and 2-hour hold, the reactor became full. It was cooled to 190°C, and a sample of the reactor slurry was collected. NMR results indicated that the DOPO conversion was about 72% at this point. The reactor was re-heated to 197-199°C, and the co-feed was conducted for another 5 hours, followed with 2.5 hour hold. The DOPO conversion was then about 93% at the end of the second co-feed, the reaction mixture was quenched with IPA and cooled slowly to ~100°C.

Once cooled, the contents of the reactor were filtered and the wetcake was then washed three times with fresh IPA and vacuum dried at 130°C.

EXAMPLES 5-10

25 Use of 6H-Dibenz[c,e][1,2]oxaphosphorin, 6,6'-(1,2-ethanediyl)bis-,
6,6'-dioxide and Ca₃Al₂(OH)_{10.8}(SiO₄)_{0.3} in epoxy laminate

In general, stock solutions of advanced resin, curative and promoter were all prepared and stored separately to facilitate experimentation. A 50 wt% o-cresolphenol epoxy novolac resin solution, NPCN® 703, obtained from Nan Ya Corporation, containing 50 wt% 2-butanone (MEK) was prepared. Durite SD-1702 novolac curing agent was obtained from Hexion Corporation. A novolac resin solution was prepared by dissolving 50 wt% SD-1702 in 50 wt% MEK solvent.

In Examples 5-6, the DiDOPO flame retardant of Example 3 (6H-Dibenz[c,e][1,2]oxaphosphorin, 6,6'-(1,2-ethanediyl)bis-, 6,6'-dioxide) containing 13.5 wt% P was ground using a jet mill to reduce the particle size of the compound to a d_{50} of about 2-4 μm prior to combining with the polymer. A flame retardant resin mixture containing 3.0 wt% P based on solids content, excluding mass contribution from the mineral filler. With the mineral filler (silica or hydrogarnet), the resin mixture contained 2.1 wt% P based on overall solids content. The resin mixture was prepared by blending 128.8 g of 50 wt% NPCN 703 solution, 62.7 g of 50 wt% SD-1702 solution, 27.4 g flame retardant and 0.083 g 2-phenylimidazole promoter. An additional 30 g MEK was added to the mixture. The novolac to promoter ratio was about 378. About 0.5-1 mL of the resin mixture was added to a hot cure plate (Thermo-electric company) at about 170-172°C. A tongue depressor was split in half lengthwise, and half of the depressor was used to move the resin on the hot plate until stiffness was noted and then lifting the resin with the flat part of the depressor until string formation ceased. The gel time was 1 minute 47 seconds, determined by the point where resin "strings" could no longer be pulled from the resin mixture and the epoxy became "tack free." The resin mixture was mixed thoroughly using a high shear mixer stirred at 5,700 rpm for about 20 minutes.

An 11 inch by 11 inch square woven glass fabric (7628 glass with 643 finish from BGF Industries) was cut to size from a large roll and stapled to wood supports (12 inches long, 1 inch wide and 1/16 inch thick) on the top and bottom ends of the fabric. The wood supports contained holes in the corners for inserting paper clips on one end for hanging the fabric in the B-stage oven. The A-stage, or resin varnish, was painted on the front and back of the fabric. Paper clips were unfolded and inserted into the both holes of one wood support. The resin-saturated fabric was hung from aluminum supports in a laboratory fume hood and allowed to drip dry for about one minute before hanging in a pre-heated (to 170 °C) forced air Blue M oven (Lab Safety Supply Inc., a unit of General Signal) for 55 seconds. The edges of the B-staged prepreg were removed by reducing the sheet dimensions to 10 inch by 10 inch. The sheet was cut into four 5 inch by 5 inch sheets and weighed before stacking the four layers of prepreg between two layers of Pacothane release film (Insulectro Corp.) and two steel plates (1/8 inch thick, 12 inch by 12 inch square dimensions). The laminate was formed in the hot press at 5,000 psig for 1 hour. The resulting laminate was 0.035 inches thick, contained 50 wt% resin and underwent 11 wt% resin overflow during pressing. Five 0.5 inch wide coupons were cut from the laminate using a diamond saw, and the coupon edges were smoothed with sandpaper. The flammability of the coupons were screened by ASTM D3801-

06 using an Atlas UL-94 burn chamber, resulting in a burn rating with 218 seconds total burn time for the two ignitions on all five coupons. Burn times for most coupons exceeded 30 seconds during the first ignition, and a second ignition was not performed. Several coupons burned slowly to the clamp.

5 Example 7 were prepared similarly to examples 5-6, but a 1:1 wt%:wt% mixture of XP-7866 and melamine polyphosphate (Melapur 200 (M-200) from BASF Corporation) was used. The resin mixture retained the targeted 3.0 wt% P based on solids content, excluding mass contribution from the mineral filler. With the mineral filler, the resin mixture contained 2.1 wt% P based on overall solids content. A UL-94 V-0 rating with 28 seconds total burn
10 time for the two ignitions on all five coupons. These results were obtained from a 0.038 inches thick laminate, containing 51 wt% resin.

The flame retardant of Example 4 (6H-Dibenz[c,e][1,2]oxaphosphorin, 6,6'-(1,2-ethanediyl)bis-, 6,6'-dioxide) containing 13.5 wt% P was ground by Fluid Energy Corporation using a jet mill to reduce the particle size of the compound to a d_{50} of about 2-4
15 μm prior to combining with the polymer. The flame retardant of Example 4 was used to prepare laminates in Examples 8-10. The laminates of Example 8-10 was prepared similarly to the laminate in Example 7 with the exception of the novolac to promoter ratio was about 794.

For the laminate of Example 8, a UL-94 V-1 rating with 79 seconds total burn time
20 was obtained for the two ignitions on all five coupons. These results were obtained from a 0.029 inches thick laminate, containing 41 wt% resin.

The laminate of Example 9 was prepared similarly to the laminate in Example 9 with the exception that 0.5 wt% of Byk Chemie W-903 dispersing agent was added prior to high shear mixing. A UL-94 V-1 rating with 53 seconds total burn time was obtained for the two
25 ignitions on all five coupons. These results were obtained from a 0.029 inches thick laminate, containing 46 wt% resin.

The laminate of Example 10 was prepared similarly to the laminate in Example 10 with the exception that 0.8 wt% of Byk Chemie W-903 dispersing agent was added prior to high shear mixing. A UL-94 V-0 rating with 43 seconds total burn time was obtained for the
30 two ignitions on all five coupons. These results were obtained from a 0.032 inches thick laminate, containing 49 wt% resin.

The total phosphorus content for Samples 5-10 was 2.1 wt% P.

Comparison of Laminates

Flame retardant and thermal properties of the laminate are shown below in Table 2. The flammability (UL-94 ratings) of the laminates was screened by ASTM D3801-06 using an Atlas UL-94 burn chamber (V-O being highest possible rating).

The Laminate Tg measurements were performed similarly to what is described in IPC method IPC-TM-650 (method 2.4.25c), using a 20°C /min temperature rate rise in N₂ with the following differences. The isothermal hold temperatures were 200°C for laminates based on DEN-438 resin, 220°C for laminates based on NPCN-703 and 250°C for laminates based on NPCN-703 resin with no flame retardant. The TA Instrument software analyzer was used to determine the glass transition temperature. In some cases a third scan was performed to determine the delta Tg between the first, second and third scans. A hole saw was used to drill out laminate sample disks of a size proportioned to fit inside a standard aluminum DSC pan. The sample edges were gently sanded to for fitting into the pan, and the most intact surface of the laminate was positioned facing the bottom of the pan. The sample weight (~40-50 mg) was recorded and a sample pan lid added using a plunger press to seal the lid onto the pan. An empty sealed pan was added to the reference platform.

The thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 TGA instrument. The TGA is connected to a PC, which provides user interface and operational system control. The temperature scale was calibrated using certified Curie temperatures of alumel and nickel reference standards. The microbalance was calibrated using certified reference weights. Both of these calibrations were performed according to the instrument manufacturers recommended procedures. The samples contained about 10 mg to 12 mg, which were heated at 10 °C/min in under nitrogen from room temperature to 500 °C in platinum sample pans. A raw data file containing the sample weight and temperature data is saved to the PC hard drive during the measurement. After the TGA measurement is finished the raw data file is analyzed for 1%, 2%, 5%, weight loss temperatures.

The total phosphorus content for Samples 5-10 was 2.1 wt% P.

TABLE 2. CHARACTERIZATION OF LAMINATES OF EXAMPLES 5 TO 10

Ex	Wt% DIDOPO	Hydro-garnet (wt%)	Silica (wt%)	M-200 (wt%)	UL-94 Rating	Total Burn Time	Tg °C (DSC)	TGA 1% loss	TGA 2% loss	TGA 5% loss
5	15.6 (Ex. 3)	-	30	-	V-0	41	159	355	375	408
6	15.6 (Ex. 3)	30 (Ex. 1)	-	-	Burn	218	163	339	360	386
7	7.9 (Ex. 3)	30 (Ex. 1)	-	7.9	V-0	28	169	327	343	371
8	7.9 (Ex. 4)	30 (Ex. 2)	-	7.9	V-1	79	175	324	343	381
9	7.9 (Ex. 4)	30 (Ex. 2)	-	7.9	V-1	53	173	309	332	375
10	7.9 (Ex. 4)	30 (Ex. 2)	-	7.9	V-0	43	173	310	334	371

Components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., another component, a solvent, or etc.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution as such changes, transformations, and/or reactions are the natural result of bringing the specified components together under the conditions called for pursuant to this disclosure. Thus the components are identified as ingredients to be brought together in connection with performing a desired operation or in forming a desired composition. Also, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, blending or mixing operations, if conducted in accordance with this disclosure and with ordinary skill of a chemist, is thus of no practical concern.

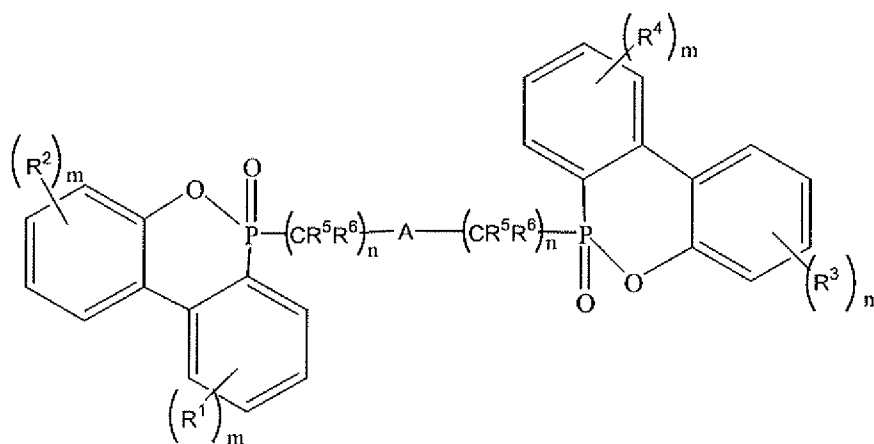
The invention described and claimed herein is not to be limited in scope by the specific examples and embodiments herein disclosed, since these examples and embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the

invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

CLAIMS:

Claim 1 A flame retardant epoxy composition comprising:

- (i) an epoxy compound;
 (ii) a compound having the following structure:



Formula I

wherein A is a direct bond, C₆-C₁₂ aryl, C₃-C₁₂ cycloalkyl, or a C₃-C₁₂ cycloalkenyl, wherein said cycloalkyl or cycloalkenyl may be optionally substituted by a C₁-C₆ alkyl;

each R¹, R², R³ and R⁴ are independently hydrogen, C₁-C₁₅ alkyl, C₆-C₁₂ aryl, C₇-C₁₅ aralkyl or C₇-C₁₅ alkaryl; or R¹ and R² or R³ and R⁴ taken together can form a saturated or unsaturated cyclic ring, wherein said saturated or unsaturated cyclic ring may be optional substituted by a C₁-C₆ alkyl;

each m is independently 1, 2, 3 or 4

each R⁵ and R⁶ are independently hydrogen or a C₁-C₆ alkyl;

each n is independently 0, 1, 2, 3, 4 or 5;

with the proviso that when A is aryl or a direct bond, n can not be 0; and

- (iii) a synthetic hydrogarnet having the empirical formula:

(A) M^{II}₃M^{III}₂(OH)_{12-4x}(SiO₄)_x wherein M^{II} is a Group IIA metal atom, M^{III} is a Group IIIA metal atom, and x is a number in the range of about 0.05 to about 1.5; or

(B) M^{II}₃M^{III}₂O_y(OH)_{12-5y}(PO₄)_y wherein M^{II} and M^{III} are as defined in (A), and y is a number in the range of about 0.05 to about 1.5; or

- (C) $M^{II}_3M^{III}_2O_y(OH)_{12-5y-4x}(PO_4)_y(SiO_4)_x$ wherein M^{II} and M^{III} are as defined in (A), wherein x is as defined in (A), and wherein y is as defined in (B), with the proviso that the sum $x + y$ is in the range of about 0.05 to about 1.5; or
- (D) $M^{II}_3M^{III}_2(OH)_{12}$ wherein M^{II} and M^{III} are as defined in (A).

Claim 2 The composition of Claim 1, wherein both n subscripts are 1 or 2; A is a direct bond; and wherein R^1 , R^2 , R^3 and R^4 are independently hydrogen or a C_1 - C_6 alkyl.

Claim 3 A flame retardant as in Claim 2 wherein said synthetic hydrogarnet has the empirical formula of (A).

Claim 4 The composition of Claim 3, wherein the compound of Formula I is 6H-Dibenz[*c,e*][1,2]oxaphosphorin, 6,6'-(1,2-ethanediyl)bis-, 6,6'-dioxide.

Claim 5 The composition of claim 3, wherein M^{II} is Ca, Ba, Mg or mixtures thereof and M^{III} is Al, Ga, Ti or mixtures thereof.

Claim 6 The composition of claim 5 wherein M^{II} is Ca and M^{III} is Al.

Claim 7 The composition of claim 6, wherein x is in the range of about 0.2 to about 0.8

Claim 8 The composition of Claim 1, wherein said epoxy compound is an polyphenol epoxy resin derived from bisphenol A, tetramethylbisphenol A, bisphenol F, bisphenol S, tetrakisphenylolethane, polybenzoxazine, resorcinol, 4,4'-biphenyl or dihydroxynaphthylene; novolac epoxy resin derived from phenol/formaldehyde novolac, cresol/formaldehyde novolac, bisphenol A novolac, biphenyl-, toluene-, xylene-, or mesitylene-modified phenol/formaldehyde novolac or aminotriazine novolac; heterocyclic epoxy resins derived from *p*-amino phenol or cyanuric acid; and aliphatic epoxy resins derived from 1,4-butanediol, glycerol or dicyclopentadiene; or mixtures thereof.

Claim 9 The composition of claim 1, further comprising a synergist, wherein said synergist is ammonium polyphosphate, melamine, melamine phosphate, melamine cyanurate, melamine pyrophosphate, melamine polyphosphate, phosphate and cyanurate derivatives of guanidine and piperazine, phosphazene compound, polyphosphazenes,

antimony oxide, antimony trioxide, antimony pentoxide, sodium antimonate, potassium antimonate, iron oxide, zinc borate or mixtures thereof. (7295)

Claim 10 The composition of claim 1, further comprising a dispersant or wetting agent.

Claim 11 The composition of claim 10 wherein said dispersant or wetting agent is: an alkylammonium salt of a polycarboxylic acid; an alkylammonium salt of a fatty acid; an alkanolammonium salt of an acidic polymer or mixtures thereof.

Claim 12 The composition of Claim 1, wherein the amount of the compound of Formula I is about 0.1 to about 100 parts by weight per 100 parts by weight of the epoxy compound; and the amount of the synthetic hydrogarnet is about 0.1 to about 100 parts by weight per 100 parts by weight of the epoxy compound.

Claim 13 The composition of Claim 1, further comprising at least one additive selected from heat stabilizers, light stabilizers, ultra-violet light absorbers, anti-oxidants, anti-static agents, preservatives, adhesion promoters, fillers, pigments, dyes, lubricants, mold releasers, blowing agents, fungicides, plasticizers, processing aids, acid scavengers, dyes, pigments, stabilizers, blowing agents, nucleating agents, wetting agents, dispersing agents, synergists, mineral fillers, reinforcing agents, whiskers, inorganic fillers, other fire-retardant additives, smoke suppressants or mixtures thereof.

Claim 14 The composition of Claim 1, further comprising a melamine polyphosphate.

Claim 15 The composition of Claim 1, wherein the d_{50} particle size of the compound of Formula I is less than about 15 microns and the d_{50} particle size of the synthetic hydrogarnet is about 0.5 to about 5 microns

Claim 16 The composition of Claim 1, further comprising a silane or fatty acid coating on the synthetic hydrogarnet.

Claim 17 The composition of Claim 16, wherein said aminosilane coating is 3-glycidyl-oxypropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 2-aminoethyl-3-aminopropyltrimethoxysilane, bis(3-triethoxysilylpropyl)amine, N-(n-butyl)-3-aminopropyltrimethoxysilane.

Claim 18 A prepreg comprising an organic or inorganic reinforcing material and the flame retardant epoxy composition of Claims 1.

Claim 19 A laminate formed from the prepreg of Claim 16.

Claim 20 A printed wiring board formed from the laminate of Claim 17.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/059723

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K21/12 C08L63/00 C08K3/34 C08K5/5313 C09K21/02
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C09K C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2010/059508 A1 (ALBEMARLE CORP [US]; GIESSELBACH MONIKA [DE]; HOEPFL WOLFGANG [DE]; HE) 27 May 2010 (2010-05-27) paragraphs [0001] - [0005], [0042] - [0044], [0050]; claims 1-8,16-22 -----	1-20
Y	US 2005/038279 A1 (DITTRICH UWE [DE] ET AL) 17 February 2005 (2005-02-17) paragraphs [0003], [0015] - [0020], [0024], [0069] - [0078], [0114] - [0122] -----	1-20
X,P	WO 2010/135393 A1 (ALBEMARLE CORP [US]; WHITE KIMBERLY M [US]; ANGELL YU LI [US]; ANGELL) 25 November 2010 (2010-11-25) page 1, line 5 - page 2, line 16; claims; examples; table 2 -----	1-20

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 20 February 2012	Date of mailing of the international search report 28/02/2012
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Martinez Marcos, V
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/059723

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO 2010059508	A1	27-05-2010	AU 2009316878 A1	27-05-2010
			CA 2742816 A1	27-05-2010
			CN 102216377 A	12-10-2011
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